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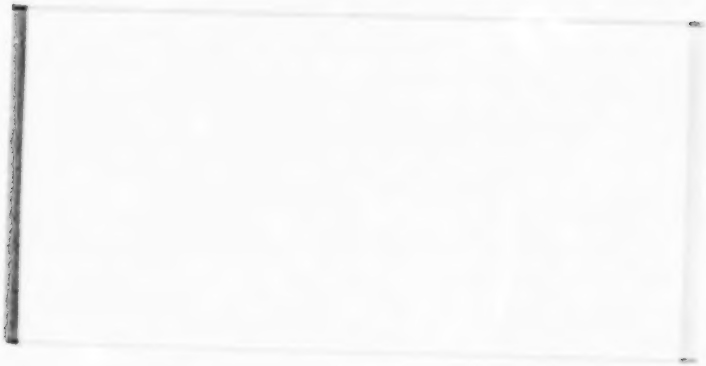

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ELECTRICAL ANHARMONICITY AND COHERENT MULTIPHOTON EXCITATION IN A LASER + dc FIELD

Report No. 85-206-K

G. F. Thomas
Process Chemistry Section
Chemical Research Department

ABSTRACT

It has recently been shown that the electrical anharmonicity of a molecule in a static electric field is responsible for the efficiency of the coherent multiphoton excitation of a vibrational mode through the participation of virtual intermediate states to a final doorway state that may lie in the quasi-continuum of rovibrational states. The theory is used to rationalize the observed enhancement in the infrared multiphoton dissociation yield of fluoroform-d in the presence of a dc field and it suggests that, at off-resonance frequencies, the field effect should vanish if the polarization vector of the linearly polarized laser beam is orthogonal to the field. On resonance the enhancement effect remains, independently of the relative orientation of the polarization vectors of the dc and ac fields.

job	file	date	report no.
31-327-650	836.3322	January 8, 1987	85-206-K

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EXECUTIVE SUMMARY

ELECTRICAL ANHARMONICITY AND COHERENT MULTIPHOTON EXCITATION IN A LASER + dc FIELD

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In the presence of a moderately strong infrared (IR) laser field, many molecules selectively absorb sufficient photons to raise them through their discrete and quasi-continua of rovibrational states to the thresholds of their various dissociation channels. This process is of great importance and has far-reaching fundamental scientific and practical significance, enabling one, for example, to control the course of unimolecular reactions, to effect the separation of isotopes exhibiting different responses towards frequency-selective laser radiation, and to induce bond- or mode-selective dissociation resulting in the tailored synthesis of desirable products. The exploitation of laser induced atomic and molecular processes to provide species monitoring and remote nonintrusive diagnostic capabilities in such diverse contexts as laboratory analytical chemistry, atmospheric pollutant chemistry, combustion in gas-, oil-, and coal-fired boilers, and in developed plasmas in fusion devices, is fast becoming an established practice.

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Current understanding of collision-free multiphoton excitation (MPE) and dissociation (MPD) processes in polyatomics is incomplete. In their review of the spectroscopic mechanisms contributing to MPD, Fuss and Kompa mention a number of the difficulties with the many theories and models that have been advanced to explain this phenomenon, not the least of which is that they only partly agree with one another. A survey of the variety of molecules that have been shown to undergo MPD suggests that a universal mechanism exists, a mechanism that should explain why there are molecules which do not undergo MPD although they are often structurally similar to others which have been successfully dissociated.

The prevailing paradigm suggests that the ascent up the harmonic stack of discrete states proceeds through the sequential near-reasonant absorption of single IR photons up to a maximum of 4 or 5, whereupon the tendency of the encroaching mechanical anharmonicity to increase the extent of detuning between the molecule and the field is compensated for by such mechanisms as power broadening, rotational band structure, and anharmonic splitting of vibrational levels. With increasing excitation energy, the restrictive compliance with spectroscopic selection rules relaxes as mechanical anharmonicity causes such an increase in the density of states that the molecule is always in resonance with the laser field. Eventually the molecule may acquire sufficient energy to dissociate through various channels.

Sazonov has recently put forward a model which predicts the enhancement of the collision-free IRMPD yield in a polyatomic subjected to an additional static magnetic field. The physical basis for this effect is the tendency of the magnetic moment of a rotating molecule to become aligned with respect to the applied magnetic field and to precess at a fixed frequency about the direction of that field. States with different orientations of the magnetic moment with respect to the wave vector of the laser field are mixed by virtue of the presence of the magnetic field and this results in an enhancement of multiphoton processes, essentially by the removal of some of the constraining effects of the selection rules governing the coupling of opposite parity states through the dipole vector operator. Additionally, Sazonov's theory predicts a strong dependence of the enhancement effect on the orientation of the applied magnetic field with respect to the propagation direction of the linearly polarized laser; the field effects should disappear if the wave vector of the laser is parallel to the magnetic field.

Van den Bergh and co-workers have reported an enhancement in the collision-free IRMPD yields of CF_2HCl on the application of an external electric or magnetic field to the reaction cell. The observed effects were interpreted as being due to a breakdown in the angular momentum selection rules in the additional strong fields, thereby leading to an increase in the density of states for MPE. These results prompted a number of theoretical investigations of the enhancement effect caused by

a static electric field with the consensus that the additional field causes energy shifts in the stationary states as well as a mixing of their parities, the net result being a richer multiphoton spectrum whose resonances are more power-broadened and blue-shifted with respect to their static field-free frequencies.

Herein the objective is to generalize a previous treatment of the effects of electrical anharmonicity on the photodymanics of a two-level system by allowing for an arbitrary orientation of the static field with respect to the polarization vector of the linearly polarized laser field, and to discuss its relevance in understanding how the vibrational modes of a polyatomic may undergo efficient coherent MPE. The theory is used to rationalize the observed enhancement in the IRMPD of CF_3D in the presence of a dc field, as reported by van den Bergh and co-workers. Deuterated fluoroform is among the potential candidate molecules for laser-mediated deuterium separation and has been intensely investigated at the Los Alamos National Laboratories, Chalk River Nuclear Laboratories, Ontario Hydro Research Division, and more recently, at the Bhabha Atomic Research Centre.

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To Dr. D. Mills
Director of Research

ELECTRICAL ANHARMONICITY AND COHERENT MULTIPHOTON EXCITATION IN A LASER + dc FIELD

G.F. Thomas

1.0 INTRODUCTION

In the presence of a moderately strong infrared (IR) laser field, many molecules selectively absorb sufficient photons to raise them through their discrete and quasi-continua of rovibrational states to the thresholds of their various dissocation channels. This process is of great importance and has far-reaching fundamental scientific and practical significance, enabling one, for example, to control the course of unimolecular reactions, to effect the separation of isotopes exhibiting different responses towards frequency-selective laser radiation, and to induce bond- or mode-selective dissociation resulting in the tailored synthesis of desirable products. The exploitation of laser induced atomic and molecular processes to provide species monitoring and remote nonintrusive diagnostic capabilities in such diverse contexts as laboratory analytical chemistry, atmospheric pollutant chemistry, combustion in gas-, oil-, and coal-fired boilers, and in developed plasmas in fusion devices, is fast becoming an established practice.

Current understanding/1,2/ of collision-free multiphoton excitation (MPE) and dissociation (MPD) processes in polyatomics is incomplete. In their review of the spectroscopic mechanisms contributing to MPD, Fuss and Kompa/3/ mention a number of the difficulties with the many theories and models that have been advanced to explain this phenomenon, not the least of which is that they only partly agree with one another. A survey of the variety of molecules that have been shown to undergo MPD suggests that a universal mechanism exists, a mechanism that should explain why there are molecules which do not undergo MPD although they are often structurally similar to others which have been successfully dissociated.

The prevailing paradigm/1,2,4/ suggests that the ascent up the harmonic stack of discrete states, refer to Fig. 1, proceeds through the sequential near-resonant absorption of single IR photons up to a maximum of 4 or 5, whereupon the tendency of the encroaching mechanical anharmonicity to increase the extent of detuning between the molecule and the field is compensated for by such mechanisms as power broadening, rotational band structure, and anharmonic splitting of vibrational levels. With increasing excitation energy, the restrictive compliance with spectroscopic selection rules relaxes as mechanical anharmonicity causes such an increase in the density of states that the molecule is always in resonance with the laser field. Eventually the molecule may acquire sufficient energy to dissociate through various channels.

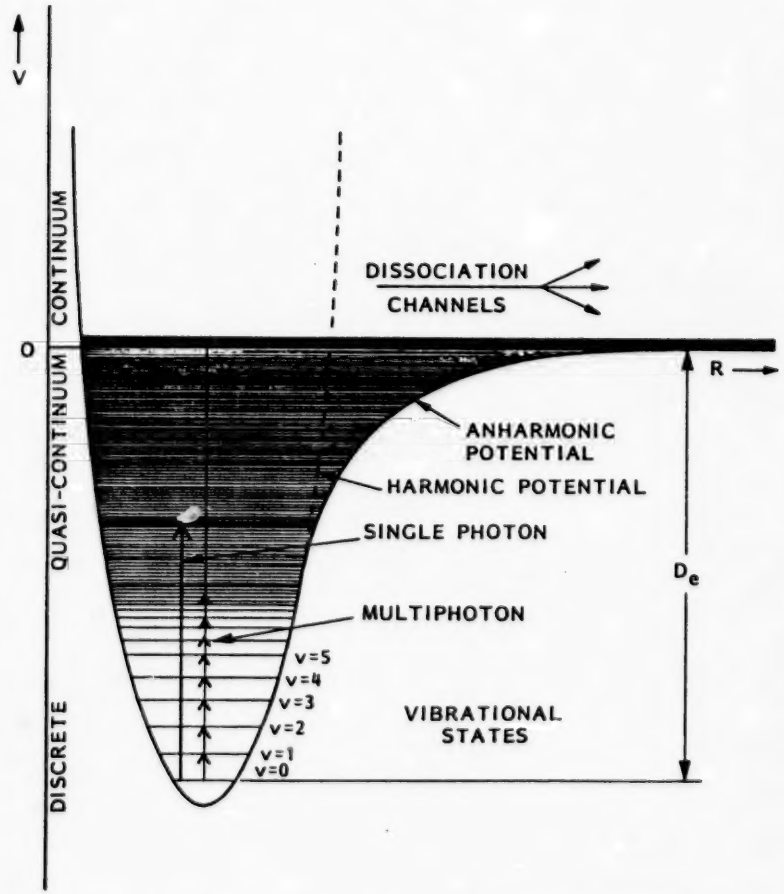

Figure 1 The potential energy V as a function of bond distance R is nearly harmonic at low energies so that the first few vibrational states v=0,1,... form an evenly spaced discrete stack. As R increases, mechanical anharmonicity results in an increased density of states. This quasi-continuum of states merges with the dissociation continuum when V exceeds the bond energy D_e. Both single-photon and multiphoton excitation of the bond are indicated schematically by the vertical arrows.

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Sazonov has recently/5/ put forward a model which predicts the enhancement of the collision-free IRMPD yield in a polyatomic subjected to an additional static magnetic field $\underline{B}$. The physical basis for this effect is the tendency of the magnetic moment of a rotating molecule to become aligned with respect to $\underline{B}$ and to precess about $\underline{B}$ at a frequency $\Omega = g\mu_n B$, where g is the gyromagnetic ratio and μ_n is the nuclear magneton. States with different orientations of the magnetic moment with respect to the wave vector of the laser field are mixed by virtue of the presence of $\underline{B}$ and this results in an enhancement of multiphoton processes, essentially by the removal of some of the constraining effects of the selection rules governing the coupling of opposite parity states through the dipole vector operator. Additionally, Sazonov's theory/5(b)/ predicts a strong dependence of the enhancement effect on the orientation of the applied magnetic field with respect to the propagation direction of the linearly polarized laser; the field effects should disappear if the wave vector of the laser is parallel to the magnetic field.

Van den Bergh and co-workers/6/ have reported an enhancement in the collision-free IRMPD yields of CF_2HCl on the application of an external electric or magnetic field to the reaction cell. The observed effects were interpreted as being due to a breakdown in the angular momentum selection rules in the additional strong fields, thereby leading to an increase in the density of states for MPE. These results prompted a number/7/ of theoretical investigations of the enhancement effect caused

by a static electric field with the consensus that the additional field causes energy shifts in the stationary states as well as a mixing of their parities, the net result being a richer multiphoton spectrum whose resonances are more power-broadened and blue-shifted with respect to their static field-free frequencies.

Herein the objective is to generalize a previous treatment/8/ of the effects of electrical anharmonicity on the photodymanics of a two-level system by allowing for an arbitrary orientation of the static field with respect to the polarization vector of the linearly polarized laser field, refer to Fig. 2, and to discuss its relevance in understanding how the vibrational modes of a polyatomic may undergo efficient coherent MPE. The theory is used to rationalize the observed enhancement in the IRMPD of CF_3D in the presence of a dc field as reported by van den Bergh and co-workers/9/. Deuterated fluoroform (CF_3D) is among the potential candidate molecules for laser-mediated deuterium separation and has been intensely investigated at the Los Alamos National Laboratories/10/, Chalk River Nuclear Laboratories/11/, Ontario Hydro Research Division/12/, and more recently, at the Bhabha Atomic Research Centre/13/.

2.0 COHERENT MULTIPHOTON EXCITATION IN A LASER + dc FIELD

The appeal to the two-level model/14/ of an atom or molecule in near-resonant interaction with a laser field is widespread. For example, van den Bergh and co-workers/9/ invoked the Rabi formula/15/ in an attempt

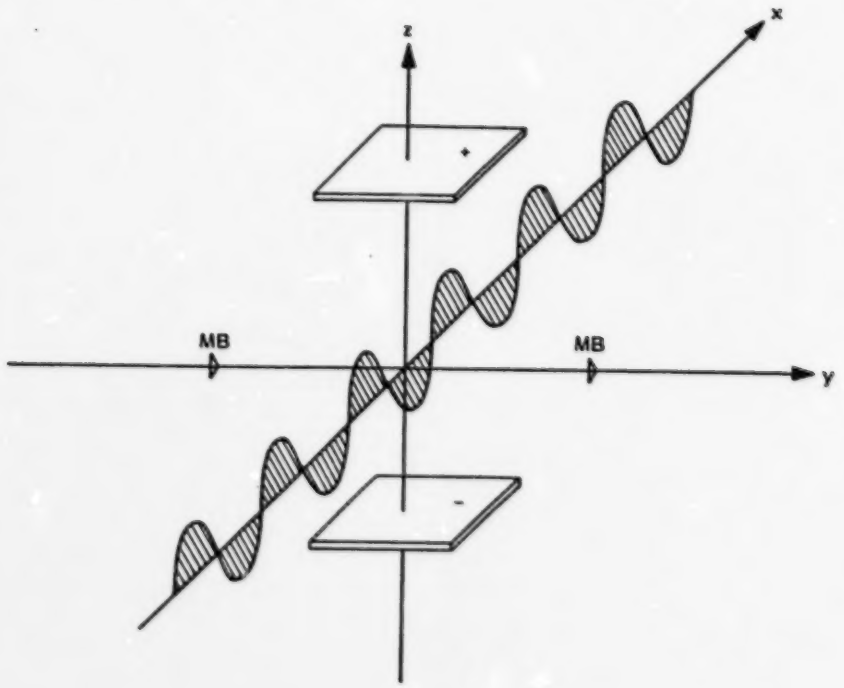

Figure 2 A schematic representation of the atomic or molecular beam (B) - laser interaction zone contained within a static electric field. The beam is propagating along the y-axis and orthogonally intersects the laser field which is propagating in the x-direction and, as displayed,the linearly polarized laser field and the applied Stark field are parallel.

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to rationalize the observed enhancement in the infrared-induced MPD of CF_3D in the presence of an additional static electric field. Bloembergen and collaborators/4/ have generalized the simple two-level Rabi system to account for the excitation of the vibrational modes of an isolated polyatomic by a continuous-wave (cw) laser, at least through the low-energy near-harmonic discrete stack to the onset of the quasi-continuum of rovibrational states. Excitation, even at moderate laser intensities, occurs through the near-resonant absorption of many photons, each photon being serially absorbed by a succession of contiguous two-level systems in accordance with the rotating-wave approximation (RWA). As a result, a sequence of non-overlapping multiphoton resonances occurs at the long-wave edge of the fundamental frequency, the width of a resonance being determined by its generalized Rabi frequency. The saturating resonances occur at integer fractions of the energy separating the ground state and the doorway state to the quasi-continuum, the interleaving states being actual rovibronic levels of the particular normal mode. The model is predicted on the assumption that the Rabi frequency for the initiating two-level system is less than the mechanical anharmonicity constant for the vibrational mode.

We have recently/8/ investigated the photodynamics of a two-level system which is orientationally polarized by a static electric field. In a sufficiently strong dc field, refer to Fig. 3, the two-level system, which in isolation has states $|i\rangle$ and $|f\rangle$ with energies ω_i and

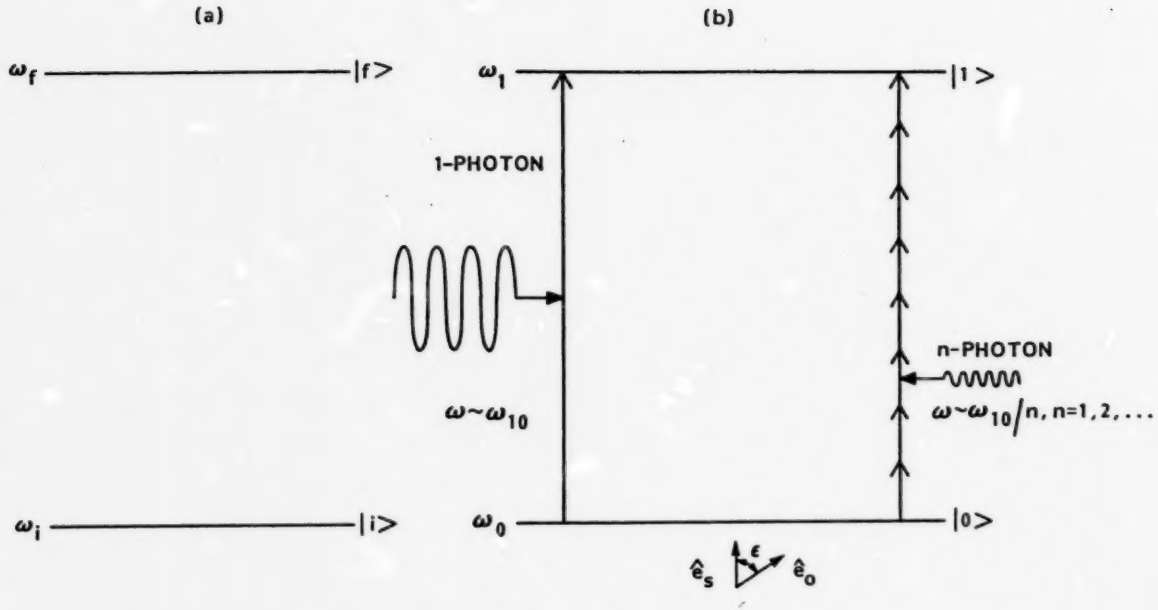

Figure 3 The interrelationship between (a) the isolated two-level system with energies ω_i and ω_f and (b) the static electric field-aligned two level system with energies ω_0 and ω_1. Excitation from the initial state $|0>$ to the final state $|1>$ can proceed through single-photon absorption from a laser field whose frequency ω is near-resonant with the level separation $\omega_{10} = \omega_1 - \omega_0$ or through a multiphoton process involving the sequential absorption of a number n=1,2... of photons, each with a frequency $\omega \sim \omega_{10}/n$, by n-1 virtual intermediate states. The ac and dc fields have polarization vectors $\hat{e}_s$ and $\hat{e}_o$, respectively,and are aligned at an angle ϵ to each other.

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ω_f, respectively, adopts/8/ as stationary states $|0\rangle$ and $|1\rangle$ with energies ω_0 and ω_1, respectively, due to the orienting action of the field. Generally $|0\rangle$ and $|1\rangle$ are of mixed parity and $\omega_{10} = \omega_1 - \omega_0$ differs from $\omega_{fi} = \omega_f - \omega_i$ so that the dc field results in a relabelling of state parities and a shift in energies. Additionally, the oriented system acquires a finite electrical anharmonicity d which vanishes in the absence of the dc field. In contrast to the generalized Rabi model of Bloembergen and co-workers/4/, absorption involves the participation of intermediate virtual states without the constraint of parity selection rules to a final doorway state whose electrical anharmonicity relative to the ground state is not excessively large but whose energy might place it well within the region characterized by a high density of states. The ability of a molecule to absorb many photons without the appeal to such mechanisms as rotational band structure, anharmonic splitting of vibrational levels, etc., in order to compensate for the increasing detuning between the molecule and field is an important feature of the model. Also, provided $d \neq 0$, it is possible to choose the ac and dc field amplitudes and the laser frequency so as to broaden the multiphoton resonances through the convolution of their subsaturating satellite peaks.

The transition probability for excitation from $|0\rangle$ to $|1\rangle$ in a field with a static component $\underset{\sim}{E}^s = E^s \hat{e}_s$, with a field strength E^s, and an oscillating component $\underset{\sim}{E}^o = E^o \hat{e}_o f(t)\cos\omega t$, with a field strength E^o and circular frequency ω, is

$$P_1^{\infty}(\omega) = \frac{1}{2} \frac{(\alpha_n \mu E^o \cos\varepsilon)^2}{\tilde{\omega}_{10}^2 + (\alpha_n \mu E^o \cos\varepsilon)^2} \qquad (2.1a)$$

in the case of cw excitation/8(a)/, i.e., when $f(t) = 1$, or

$$P_1^{\infty}(\omega) = \exp(-\tilde{\omega}_{10}^2 \tau_p^2/2\pi) \sin^2[\tfrac{1}{2}\alpha_n \mu E^o \tau_p \cos\varepsilon] \qquad (2.1b)$$

in the case of Gaussian-pulsed excitation/8(b)/, i.e., when $f(t) = \exp(-t^2\pi/\tau_p^2)$, where $\tilde{\omega}_{10} = \omega_{10} - n\omega$ is the detuning frequency, τ_p is the epochal duration of the pulse, $\langle 0|\mu_{3,m}|1\rangle + E^s\bar{\alpha}_m$ is the transition dipole matrix element, $\mu_{3,m}$ and $\bar{\alpha}_m = \alpha_{33,m}$ are the field-directed components of the permanent dipole moment vector and the polarizability tensor, respectively, in the molecule-fixed co-ordinate system, ε is the angle between the unit polarization vectors $\hat{e}_s$ and $\hat{e}_o$, and the function α_n is defined by

$$\alpha_n(d, E^o, \varepsilon, \omega) = (2n/dE^o\cos\varepsilon)J_n(dE^o\cos\varepsilon/\omega), \qquad (2.2)$$

where the J's are Bessel functions of the first kind. The electrical anharmonicity $d = \mu_{00} - \mu_{11}$, where $\mu_{00} = \langle 0|\mu_{3,m}|0\rangle + \bar{\alpha}_m E^s$ and $\mu_{11} = \langle 1|\mu_{3,m}|1\rangle + \bar{\alpha}_m E^s$, is the difference in the permanent dipole moments of the static field-oriented two-level system; d vanishes in the absence of the static field. The index n=1,2... on the right in

Eqs. (2.1) and (2.2) pertains to the proresonant phasors oscillating at the fundamental (n=1) and overtone (n=2,3...) frequencies of the laser field retained in applying the RWA and which are assumed to contribute significantly to the transition rates of the two coupled states $|0\rangle$ and $|1\rangle$ of the static field-oriented system. If $d = 0$, $\alpha_n = \delta_{n,1}$ so that only single-photon absorption occurs. Generally $d \neq 0$ with which n = 1,2... and n-photon absorption occurs. However, if dE^o is arbitrarily large then $\alpha_n \to 0$ and consequently at off-resonance frequencies $P_1^{\infty}(\omega)$ vanishes. Also, if $\varepsilon = \pi/2$ then at off-resonance frequencies $P_1^{\infty}(\omega)$ vanishes and not alone does the field enhancement effect disappear but in fact no absorption occurs. On resonance, $P_1^{\infty}(\omega) = 0.5$ in the case of cw excitation or following a train of identical phase-coherent Gaussian pulses, independently of ε.

3.0 ENHANCED IRMPD OF FLUOROFORM-d IN A dc FIELD

One may view the observed/9/ enhancement of the MPD yield of CF_3D as being due to the efficiency of multiphoton absorption by the field-oriented system from the ground state $|0\rangle$, through the participation of intermediate virtual states, to a final doorway state $|1\rangle$ whose energy may place it within the quasi-continuum of rovibrational states, subject to the proviso that dE^o is not too large. In contrast, the generalized Rabi model accounts for the absorption of several photons through real states to the onset of the quasi-continuum, subject to the parity-governed selection rules.

One of the predictions of Sazonov's model/5(b)/ is a strong dependence of the field effect on the angle between the laser polarization vector for linearly polarized light and the applied magnetic field; if the two are orthogonal then Sazanov's model would indicate that the magnetic field would not affect the IRMPD yield. Van den Bergh and co-workers/9/ were not able to verify this experimentally for CF_3D in a magnetic field. However, they did investigate the effect in their electric field experiments and found that whether the dc field was parallel or perpendicular to the laser polarization direction, the enhancement was the same although precise details on the strength of either the laser or static field were not reported. As discussed above, the model we have proposed for the enhancement effect in an electric field, like Sazonov's model, would indicate that the effect should vanish at off-resonance frequencies if $\varepsilon = \pi/2$. In practice, $\varepsilon = \pi/2 \pm \varepsilon'$, where the misalignment ε' is small, which when substituted into Eq. (2.1) effectively scales E^o by $\varepsilon' \ll 1$ and while this would result in a smaller fraction f of molecules dissociated per laser pulse in the irradiation zone, the relative change in yield induced by the field, defined as $R = f(E^s)/f(0)$, would not necessarily be affected, assuming f to be proportional to $P_1^{\infty}(\omega)$. On resonance the system saturates and the enhancement effect remains, independently of the relative orientation of the polarization vectors of the ac and dc fields.

In the experiments on CF_3D reported by van den Bergh and co-workers/9/ $E^s << E^o$ and the dc field may not be sufficiently strong to align the dipole moment along a fixed direction. If that is the case then the randomly oriented dipole moment operator is $\mu_{3,m}^2 (E^s/3kT) + \bar{\alpha}_m E^s$, where k is Boltzmann's constant, T is the absolute temperature, and $\bar{\alpha}_m$ is the mean polarizability of the system. Under these circumstances d will generally be small, its magnitude being a measure of the extent to which the orienting action of E^s dominates over the randomizing effect of T. Ultimately when $E^s = 0$, $d = 0$ and then only single-photon absorption becomes possible for the isolated two-level system. Rather than serially applying the Rabi formula to account for cw MPE one may apply its generalization/16/ that includes the effects of the dc field and is given by

$$P_f^\tau(E^s,\omega) = \frac{1}{2} \frac{4\mu^2 (E^s + E^o/2)^4}{\tau^{-2}(E^s + E^o/2)^2 + (E^s\omega_{fi} + E^o\tilde{\omega}_{fi}/2)^2 + 4\mu^2(E^s + E^o/2)^4}, \quad (3.1)$$

where τ is a mean relaxation time, $\mu = \langle i | \mu_z | f \rangle$ with μ_z being the component of the dipole moment operator in the direction of the parallel polarization vectors of $\underset{\sim}{E}^s$ and $\underset{\sim}{E}^o$, and $\tilde{\omega}_{fi} = \omega_{fi} - \omega$ is the detuning. The relative change in yield of the number of molecules that have absorbed a single photon is given by $R = P_f^\tau(E^s,\omega)/P_f^\tau(0,\omega)$, i.e.,

$$R = \frac{4\mu^2(E^s + E^o/2)^4 \{\tau^{-2} + \tilde{\omega}_{fi}^2 + (\mu E^o)^2\}}{(\mu E^o)^2\{\tau^{-2}(E^s+E^o/2)^2 + (E^s\omega_{fi} + E^o\tilde{\omega}_{fi}/2)^2 + 4\mu^2(E^s+E^o/2)^4\}} \quad (3.2)$$

Three limiting forms of Eq. (3.2) are of interest, viz., (i) as $E^o \sim \infty$, $R \sim 1$ so that R decreases with increasing laser field strength as displayed in Fig. 2 of Gozel et al./9/; (ii) as $(E^s)^2 \sim \infty$, $R \sim (2\mu E^s)^2/\{\tau^{-2} + \omega_{fi}^2 + (2\mu E_s)^2\}$ so that R saturates with increasing $(E^s)^2$ as displayed in Fig. 4 of Gozel et al./9/; (iii) as $\tau \sim 0$, $R \sim 1$ so that the enhancement effect diminishes with decreasing relaxation time as displayed in Fig. 5 of Gozel et al./9/, although ultimately the onslaught of intra- and intermolecular relaxation will ensure that both $P_f^\tau(E^s,\omega)$ and $P_f^\tau(0,\omega)$ vanish.

4.0 CONCLUSIONS

The argument presented here identifies the finite electrical anharmonicity of the dc field-aligned fluoroform-d molecule (or indeed any molecule) as the property responsible for its ability to absorb many photons from either a cw or Gaussian-pulsed laser, through the participation of virtual intermediate states, to a doorway state from which it may ascend the quasi-continuum of rovibrational states. In the absence of the dc field, the electrical anharmonicity vanishes and the pathway to the quasi-continuum is described by the generalized Rabi model of Bloembergen and co-workers. A simple two-level model which

incorporates the effects of a weak dc field is in qualitative agreement with the observations of van den Bergh and associates on fluoroform-d.

The theory suggests that the enhancement effects should vanish at off-resonance frequencies if the polarization vector of the linearly polarized laser is orthogonal to the dc field. This prediction is not necessarily at odds with the measurements of van den Bergh and co-workers on fluoroform-d. A small misalignment of the polarization vectors could yield a finite (>1) relative change in IRMPD yields although the fraction of molecules dissociated per laser pulse would be small. Further, on resonance the field-aligned two-level system saturates, independently of the relative orientation of the polarization vectors of the ac and dc fields.

As discussed more fully elsewhere/8/, the Lorentzian line shape given in Eq. (2.1a) and the Gaussian line shape given in Eq. (2.1b) for cw and Gaussian-pulsed excitation, respectively, may be accompanied by oscillatory fringes on appropriate choice of the ac and dc field amplitudes and the laser frequency. These windows in the line shape, corresponding to a reduction in multiphoton absorption, may be desirable as in isotope separation applications where the electrical anharmonicities of the

isotopic species will generally differ so that by the right choice of static and laser field parameters one may preferentially excite a specific isotope.

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